Absorption of Helium and other Gases under the Electric Discharge.

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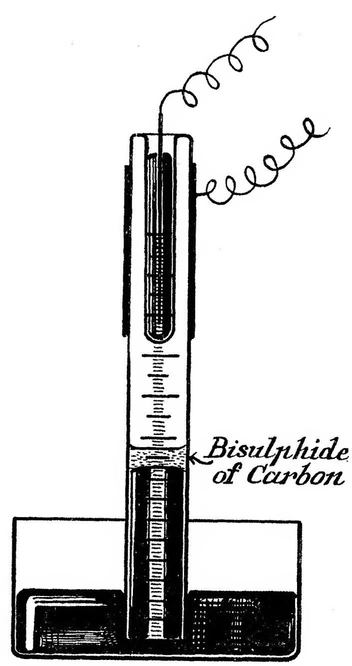
Berthelot announced in 1896 that he had succeeded in observing an absorption of argon, and later of helium, when these gases were submitted to the silent electric discharge, in the presence of either benzene or bisulphide of carbon: further, that the gases could be extracted by heat from the solid substances deposited on the walls of the vessel. The experiments were regarded as proving that argon and helium were after all capable of entering into chemical combination. I shall confine discussion to the supposed interaction of helium and carbon bisulphide. Berthelot obtained more definite results with this reagent than with benzene.*

At the time they were published, these results were not generally accepted, and, so far as I have been able to learn, they have not been more favourably regarded since. Berthelot, however, adhered to them in his 'Traité Pratique de l'Analyse des Gaz,' published in 1906, about the time of his death, and other experimenters have not produced definite evidence against them. The subject cannot be considered unimportant, and I have long felt that the experiments ought to be repeated. This has now been done, with results altogether negative.



The helium used was freed from hydrogen by explosion with excess of oxygen, and then purified by cooled charcoal. The gas stood over mercury in a Siemens tube as shown in the figure. This tube was graduated, and on the mercury floated a layer of bisulphide of carbon. The induction coil used was worked by a mercury turbine interrupter, and resistances were interposed in the primary circuit to reduce the spark it was capable of giving to about $\frac{1}{2}$ inch. This was to avoid danger of piercing the

* 'Annales de Chimie et de Physique,' 1897, Series 7, vol. 11, p. 15.

glass. When the discharge is passed, solid decomposition products of disulphide of carbon are deposited on the walls of the glass tube, and the quantity of liquid bisulphide diminishes.

In the final and most prolonged experiment, on which reliance is chiefly placed, about 2·5 c.c. of pure helium was placed in a small Siemens tube with bisulphide of carbon, which brought up the volume (at room temperature) to 4 c.c.

The coil was kept in continuous action for 120 hours; during this period the volume reading oscillated a little around its initial value owing to inevitable variations of temperature, to which of course the vapour-tension of the bisulphide is very sensitive. These variations, however, did not show any tendency to one direction rather than the other, and at the end of the 120 hours' sparking the volume actually read was 4·2 c.c. There was no tendency whatever to contraction. In the course of this experiment about 0·75 c.c. of liquid bisulphide of carbon was converted into solid products.

Since no contraction had occurred, there did not seem much prospect of extracting helium from this solid material. It was thought desirable, however, to test the point independently. The Siemens tube was well washed out with air, and attached to a small vacuum tube and charcoal reservoir and exhausted. The deposit was heated to the softening point of the glass containing it, but when the charcoal was cooled all gas was absorbed, so that the spectrum tube could not be excited. The charcoal was allowed to warm up, and the spectrum watched as it was cooled again. Nothing could be seen of the helium line at any stage.

It was not thought necessary to estimate precisely the sensitiveness of this test as carried out, for it was certainly more than enough. Nothing like 1/10 c.c. of helium can have been extracted, for any such quantity would have been glaringly conspicuous.

As a test of the methods of manipulation employed, I tried the absorption of nitrogen by bisulphide of carbon under the same conditions.

The initial volume (nitrogen + carbon disulphide vapour) was 4 c.c. On passing the discharge, a slow but steady contraction occurred, the volume diminishing in 29 hours to 2·4 c.c. The mercury had then risen to a level in the tube which was obscured by the black deposit of decomposition-products, and the experiment was discontinued. The rate of contraction with helium (if any) was certainly not more than one-seventieth part of this.

My results are, then, quite definitely negative, and the conditions apparently not materially different from those of Berthelot's experiments. Yet the latter are so minutely described, and so apparently conclusive, that even with this experience it is difficult not to feel some hesitation in

rejecting them. If any future experimenter should succeed in getting the absorption, I should be disposed to regard it as mechanical rather than chemical, like the undoubted absorption of helium by aluminium scattered from the cathode of a vacuum discharge tube.* The solid decomposition-products of carbon bisulphide are deposited on the glass in a compact film, and gas may be absorbed mechanically as in the case mentioned.

It is known that phosphorus under the influence of electric discharge is capable of absorbing gases. The method has been used by Sir Oliver Lodge for exhausting his vacuum valves.† The considerations just mentioned raise the question whether this action is chemical or mechanical. For the discharge passing through phosphorus vapour converts it into the red modification, which is deposited as a coherent film on the glass, and mechanical retention of gas under these circumstances is quite conceivable. I pass to some experiments designed to test the question.

The discharge vessels used were oval bulbs of about 50 c.c. capacity. These were provided with aluminium wire electrodes, and were connected to an apparatus for admitting any desired gas in small successive doses, and to a siphon vacuum gauge reading to 1 mm.

The first experiments were made with nitrogen; 50 mgrm. of phosphorus were placed in the discharge vessel, which was highly exhausted, and a dose of nitrogen (1·43 c.c.) admitted. The discharge was passed, and in about five minutes the manometer indicated that all gas had been absorbed. This was repeated till four doses had been absorbed. The action had then become slower, and the bulb was strongly heated with a Bunsen flame. This did not liberate any of the absorbed gas, but it reconverted the red phosphorus deposited on the walls to yellow phosphorus. Two more doses of nitrogen were admitted and absorbed. Heating was repeated. Finally, one more dose was admitted, and could only partially be absorbed. The total absorption amounted to 10 c.c., or 200 c.c. per gramme of phosphorus. The tube was finally heated to incipient softening of the glass, but the manometer did not indicate any liberation of gas.

Similar experiments were made with hydrogen. The amount of absorption effected was at the rate of 84 c.c. of hydrogen per gramme. Here, again, the gas could not be extracted by heat. This circumstance, considered in connection with the comparatively large quantity of gas absorbed, justifies the conclusion that nitrogen and hydrogen both enter into chemical union with phosphorus under these conditions. There is scope for an interesting chemical research in examining the solid products.

* Soddy and Mackenzie, 'Roy. Soc. Proc.,' 1907, A, vol. 80, p. 92.

† British Patent No. 25047, 1905.

Experiments of a similar kind were made with pure helium in place of hydrogen or nitrogen. In this case, too, a distinct absorption of gas was observed, but it was very slight, and of a smaller order of magnitude than in the previous case.

Four grammes of phosphorus were placed in a 50 c.c. discharge vessel, which was provided with a manometer. Helium was admitted to 13 mm. pressure, and the tube sealed off. After 70 hours' run the pressure had fallen to 3 mm., and could not be made to fall further. This represents an absorption of 0·16 c.c. per gramme, as compared with 84 c.c. for hydrogen, and 200 c.c. for nitrogen. On heating the helium was nearly all liberated again, as indicated by the manometer.

The behaviour of helium is, then, sharply distinguished from that of hydrogen or nitrogen. The absorption is only 1/500 part, or less, and the gas can be liberated by heat, whereas nitrogen or hydrogen are firmly retained. I conclude, then, that helium is mechanically, and hydrogen or nitrogen chemically, retained by phosphorus.

Summary.

Attempts to repeat Berthelot's absorption of helium by carbon bisulphide under the influence of the silent discharge have given absolutely negative results.

Helium is slightly absorbed by phosphorus under electric discharge, though in much less quantity than nitrogen or hydrogen. The absorption in the former case is regarded as mechanical, in the latter as chemical.